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Bis(pentalene)dititanium Chemistry: C-H, C-X and H-H Bond Activation*

Nikolaos Tsoureas[1], Jennifer C. Green[2*], and F. Geoffrey N. Cloke[1*]

[1]School of Life Sciences, Department of Chemistry, University of Sussex, Falmer, Brighton, BN1 9QJ, United Kingdom. [2] Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, United Kingdom.

Abstract:

The reaction of the bis(pentalene)dititanium complex $Ti_2(\mu{:}\eta^5,\eta^5\text{-}Pn^\dagger)_2$ ($Pn^\dagger = C_8H_4(1,4\text{-}Si^iPr_3)_2$) (**1**) with the N-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene results in intramolecular C–H activation of an isopropyl substituent to form a tucked-in hydride (**3**). Whilst pyridine will also effect this cyclometallation reaction to form (**5**), the pyridine analogue of (**3**), the bases 1,2,4,5-tetramethyl-imidazole, 2,6-lutidine, DABCO or trimethylphosphine are ineffective. The reaction of (**1**) with 2,6-dichloro-pyridine affords crystallographically characterised (**6**) which is the product of oxidative addition of one of the C-Cl bonds in 2,6-dichloro-pyridine across the Ti-Ti double bond in (**1**). The tucked-in hydride (**3**) reacts with hydrogen to afford a dihydride complex (**4**) in which the tuck-in process has been reversed; detailed experimental and computational studies on this reaction using D_2, HD or H_2/D_2 support a mechanism for the formation of (**4**) which does not involve σ-bond metathesis of H_2 with the tucked-in C-H bond in (**3**). The reaction of (**3**) with ^{t}BuCCH yields the corresponding acetylide hydrido complex (**7**), where deuteration studies show that again the reaction does not proceed *via* σ-bond metathesis. Finally, treatment of (**3**) with HCl affords the chloro-derivative (**9**) $[(NHC)Ti(\mu\text{-}H)Ti\{(\mu,\eta^5{:}\eta^5)Pn^\dagger\}_2Cl]$, whereas protonation with $[NEt_3H]BPh_4$ yielded a cationic hydride (**10**) featuring an agostic interaction between a Ti centre and an ^{i}Pr Me group.

Introduction:

The organometallic chemistry of the group 4 transition metal triad has played a pivotal role in the advancement of the field[1] with landmark discoveries such as the agostic interaction between a C-H bond and a Ti centre.[2] Similarly, the pursuit and isolation of the 'elusive' titano/zircono/hafnocenes has been an important development in the history of the field and has opened avenues towards the activation of many important small molecules.[3] More recently, the participation of group 4 metallocene fragments in frustrated Lewis acid/base pairs and the subsequent activation of a host of substrates has been reported.[4] Furthermore, their application as polymerisation pre-catalysts is still an ongoing area of intense research.[5] Despite these advancements, only a handful of isolable compounds containing group 4 metal-metal bonds are known.[6] Our group has reported on the synthesis[7] and subsequent reactivity[8] of one such complex: $[Ti_2\{(\mu,\eta^5{:}\eta^5)Pn^\dagger\}_2]$ (**1**) ($Pn^\dagger$ = $\{1,4\text{-}Si^iPr_3\}_2\text{-}C_8H_4$) (Scheme 1). As part of these investigations we have recently reported on the activation of both C-H and subsequently H-H bonds facilitated by the reaction of (**1**) with the free carbene 1,3,4,5-tetratmethyl-imidazol-2-ylidene (**2**) (Scheme 1).[9] Interestingly the 'tuck-in' hydride compound (**3**), reacts with H_2 to reconstitute the cyclometallated C-H bond and form the dihydride complex (**4**) (Scheme 2), but not *via* a σ-bond metathesis mechanism, as demonstrated by deuterium labelling experiments (Scheme 2), and computational investigations. (**3**) and (**4**) are rare examples of titanium hydride complexes, and in this paper we present further studies on: (*a*) understanding the promotion

* Dedicated to Dick Andersen in celebration of his 75th birthday and wishing him many more

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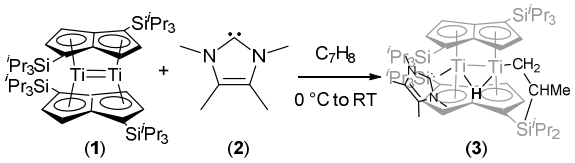
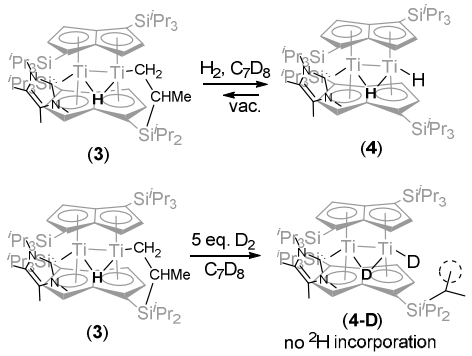
of the C-H activation leading to the formation of (**3**); (*b*) the reactivity of (**3**) with HY (Y = H, D and mixtures thereof) and further evidence against the σ-bond metathesis mechanism, *vide supra* ; (*c*) the reactivity of (**3**) towards ^{t}BuCCH (*ie* an acidic C-H bond), and with protic acids.



Scheme 1: NHC induced cyclometallation of (**1**)



Scheme 2: Formation of a dihydride syn-bimetallic Ti_2 complex by hydrogenolysis of (**3**)

Results and Discussion:

Reactivity of (**1**) towards other bases:

In our original communication, we briefly discussed the importance of using the NHC (**2**) in promoting the cyclometallation reaction leading to (**3**) (Scheme 1),[10] and have subsequently examined other bases. When the structurally related but less basic 1,2,4,5-tetramethyl-imidazole was mixed with (**1**) in C_7D_8, no reaction was observed, even at elevated temperatures (up to 90 ˚C). The reaction of (**1**) with the stronger base pyridine does yield (**5**) (the pyridine analogue of (**3**)), as evidenced by preliminary structural data (see ESI); however, this compound displays extremely complex ^{1}H NMR behaviour in solution which, despite our best efforts, we have been unable to rationalise thus far so (**5**) will not be discussed further here.[11] The somewhat more hindered 2,6 lutidine shows no reactivity towards (**1**) up to a temperature of 80 ˚C in C_7D_8;[12] neither an excess of PMe_3 or DABCO react with (**1**). These observations suggest that, for the cyclometallation reaction leading to (**3**) to occur, (i) a strong σ-donor base and, equally importantly (ii) a base with a planar shape are required.

We have also studied the reaction of (**1**) with 2,6-dichloro-pyridine, as a less sterically demanding version of 2,6 lutidine. Addition of C_6D_6 or C_7D_8 to a 1:1 mixture of (**1**) and 2,6-dichloro-pyridine and in a Young's NMR tube resulted in the instantaneous formation of a deep red solution, and NMR spectroscopy revealed the very clean formation of a new species in quantitative yield (Scheme 3).

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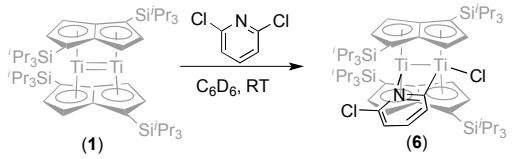

Scheme 3. Reaction of (**1**) with 2,6-dichloro-pyridine

This new complex (**6**) displays no hydridic resonances, but features two inequivalent Pn† ligand environments (as evidenced by the appearance of 8 doublets assigned to the C-H Pn† protons and further corroborated by $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$-NMR spectroscopy), and resonances associated with an asymmetric pyridyl ligand. Interestingly a doublet ($^3J_{HH}$ = 7.01 Hz) at 10.02 ppm ($\delta(C_6D_6)$) assigned to a pyridyl proton was observed. Crystals of (**6**) suitable for a single crystal X-ray diffraction analysis could be grown either by cooling a saturated n-pentane solution at -35 ˚C or by slow evaporation of toluene under dynamic vacuum. An ORTEP diagram of the molecular structure of (**6**) is shown in Figure 1.

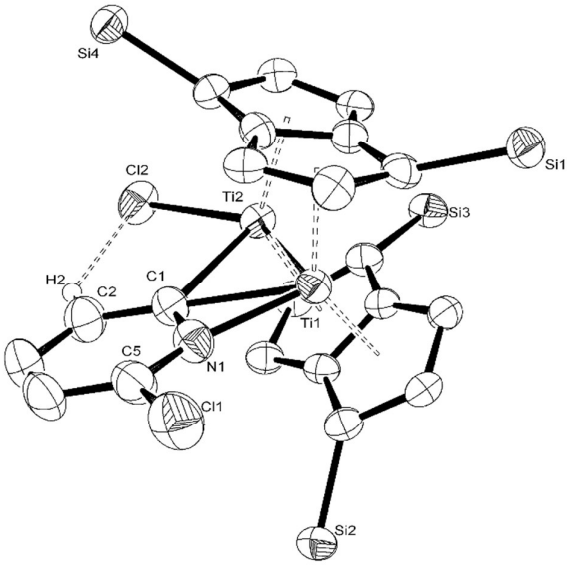

Figure 1: ORTEP diagram of the molecular structure of (**6**) showing 50% probability ellipsoids (H atoms and ^{i}Pr groups have been removed for clarity). Selected bond lengths (Å) and angles (°): Ti1-C1: 2.298(5), Ti1-N1: 2.060(4), Ti1-Ti2: 2.5064(12), C1-Ti2: 2.423(6), Ti2-Cl2: 2.4087(15), N1-C1: 1.362(7), N1-C5: 1.314(8); Ti2-C1-Ti1: 64.08(15), C1-N1-Ti1: 81.6(3), Cl2-Ti2-C1: 87.30(14), C1-Ti1-N1: 35.92(19), Ti2-Ti1-C1: 60.41(15), Ti1-Ti2-C1: 55.51(13), Ti2-C1-N1: 126.4(4), Cl2-Ti2-C1: 87.30(14).

As can be seen from Figure 1, complex (**6**) is the product of the oxidative addition of one of the C-Cl bonds in 2,6-dichloro-pyridine across the Ti-Ti double bond in (**1**). The molecular structure of (**6**) is consistent with the solution NMR spectroscopic data discussed above. The interaction between atoms H2 and Cl2 (2.39(6) Å) (Figure 1) observed in the solid state structure of (**6**) accounts for the observed down-field shift (δ 10.02) of this proton observed in the ^{1}H-NMR spectrum of (**6**) and therefore seems to be persistent in the solution state. The distance of this interaction is more akin to an

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intermolecular hydrogen bond, like the one crystallographically determined in [*trans*-$PtCl_2$(di-isopropyl-phosphino-*N*-amino-piperidine)$_2$] (2.37(5) Å),[13] rather than a mere short contact.[14]

The Ti-Ti bond (2.5064(12) Å) has been retained but has lengthened in comparison to (**1**) (2.399(2) Å)[7] and is characteristic of a single bond. It has to be noted that it is slightly shorter than the one found in (**3**) (2.5610(8) Å)9, and significantly shorter than the ones found in complexes of the general formula $\{(\mu,\eta^5{:}\eta^5)Pn^{\dagger}\}_2[Ti(EPh)]_2$ (E = S, Se, Te) (2.6519(9), 2.6581(15) and 2.6530(9) Å respectively),8[d] which also derive from the oxidative addition of PhEEPh across the Ti=Ti double bond in (**1**). Interestingly, the Ti-N bond distance is significantly shorter than a dative N→Ti bond (N = pyridine,[15,16] Me_3[ane]N_3[16]), which is typically found in the range between 2.2-2.4 Å, and falls between the bond lengths found for terminal (longer) and bridging (shorter) Ti amide bonds.

Whilst a structurally characterised mononuclear titanium complex featuring a $\{(\kappa^2\text{-NC})_{pyridyl}\}$ ligand has recently been reported,[17] (**6**) is the first structurally authenticated example of a di-titanium compound featuring such ligation. $\{(\kappa^2\text{-NC})_{pyridyl}\}$ has also been seen in Zr complexes,[18] complexes of group 3 metals (Sc[19], Y[20]) as well as vanadium,[21] molybdenum,[22] rhenium[23] and group 8 (Ru, Os)[24] metal complexes. In all these structurally characterised examples, the *ortho*-cyclometallation of the pyridine heterocycle leads to the perturbation of the aromatic system, as is the case in (**6**) (N1-C5: 1.314(8) Å *vs* N1-C1 1.362(7) Å; all other bond lengths, including N1-C1, are similar within esd's). It should be noted that in all the previous structurally characterised examples the N-C bond distances are similar within esd's, unlike the case of (**6**). This is most likely due to the involvement of the second metal centre.

The best analogy for (**6**) can be found in the case of $[Ti(N_2O^*)(CH_2Ph)]_2$, (N_2O^* = 3,3-dimethyl-1,5-diaza-8-oxacyclodecane) where a metallaziridine has been formed as a result of C-H activation of the macrocyclic framework.[25] In this case each Ti metal centre features two amide bonds in its coordination sphere; one bridging with a Ti-N bond distance of 2.106(2) Å and a terminal one with a corresponding length of 1.968(2) Å.

Reactivity of (**3**) with HY (Y = H, D) and mixtures thereof:

As mentioned above, (**3**) reacts with H_2 to produce the di-hydride complex (**4**) which features terminal and bridging hydrides. Replacing H_2 for D_2, produces its isotopologue (**4-D**) where no deuterium incorporation is observed in the previous 'tucked-in' methyl group of (**3**) (Scheme 2), strongly suggesting that the transformation of (**3**) to (**4**) under H_2 (or D_2) does not proceed *via* σ-bond metathesis. Furthermore, the conversion of (**3**) to (**4**) is pressure dependent. We now report further experimental and computational studies on the conversion of (**3**) to (**4**).

Adding 5 eq of HD to an C_7D_8 solution of (**3**) resulted in the formation of isotopomers as evidenced by ^{1}H-NMR spectroscopy at 0 ˚C (Figure 2a-left).[26] The (overall) relative integration of the peak corresponding to the bridging hydride of 0.5H is consistent with a 1:1:1:1 ratio of the four possible isotopomers, since two of them have deuterium in the bridging position. (Figure 2b-right).

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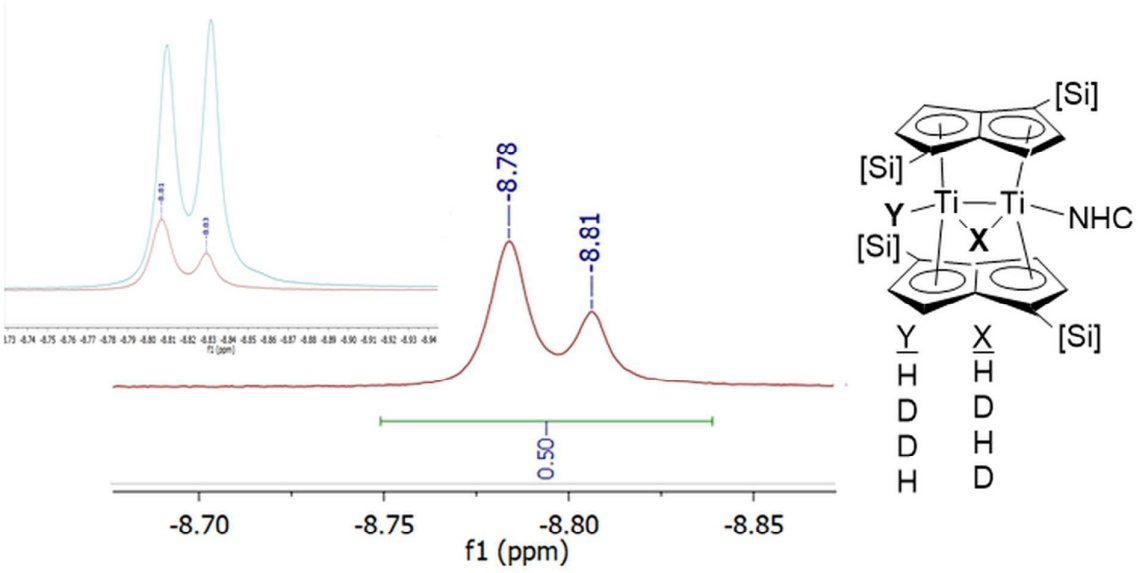

Figure 2: From left to right (a): Bridging hydride region in the ^{1}H-NMR spectrum (δ C_7D_8) of the reaction of (**3**) with 5 eq, HD at 0 ˚C showing the formation of isotopomers - the insert shows the overlay of the corresponding peaks of (**4**) (green) and (**4-XY**; X,Y = H, D) (red); (b): isotopomers of (**4**) ([Si] = Si^{i}Pr$_3$, NHC = 1,3,4,5-tetratmethyl-imidazol-2-ylidene (**2**)).

When the reaction was performed adding 5 eq of a 1:1 mixture of H_2/D_2, (*ie* 2.5 equivalents of each gas relative to (**3**)) again isotopomers were observed; in this instance though, the integration of the bridging hydride peak of 0.75H suggests that under these conditions the formation of 0.25 eq of the [TiHTiD] isotopomer is formed *via* exchange. Such an exchange was confirmed by the reaction of a freshly prepared solution of (**4-H**) with *ca* 2 eq. of D_2 (administered *via* a Toepler line, *ca* 0.34 bar overpressure) leading to the slow formation over a week of (**4-D**) as evidenced by ^{1}H-NMR spectroscopy. Furthermore, when the volatiles of this reaction were vacuum transferred the presence of HD was observed in solution. On the other hand, when equimolar amounts of *in-situ* prepared (and freeze-thaw degassed prior to mixing) (**4-H**) and (**4-D**) are mixed, under an atmosphere of Ar or N_2, no such exchange leading to the formation of isotopomers occurs. In order to gain a better understanding of these experimental observations, we decided to investigate the exchange between (**4-H**) and D_2 leading to (**4-D**) computationally.

Calculations were performed using the ADF modeling suite at the BP86/TZP level of theory (details are given in the ESI).[27] The reaction of (**3**) with H_2 to form (**4**) has been calculated previously9 to have ΔG = -31 kJ/mol and ΔG^{act} = 84 kJ/mol. The reaction may be reversed under reduced pressure the calculated activation energy being 115 kJ/mol.

To account for the presence of mixed H/D isotopomers, exchange of H_2 (H1-H2) has been investigated with $Ti_2Pn_2(C_3N_2H_4)H(\mu\text{-}H)$ (***4***) as a model (*ie* no Si^{i}Pr$_3$ or Me groups). A possible pathway has been found which exchanges with the terminal H3. The reaction pathway is illustrated in Figure 3 and key interatomic distance given in Table 1. A very weakly bound intermediate has been found on the reaction pathway in which the terminal H3 has moved to the "side" of the molecule and H_2 is bound in the "front", **Int**. The transition state on the frontal approach, **TS1**, has a free energy of activation of 110 kJmol^{-1}. The H-H bond is barely lengthened at this point with the H1-H2 distance being 0.76 Å. The main change is the movement of the exchanging H3 the Ti-Ti-H angle increasing from 116° to 119°. The intermediate, **Int**, is barely distinguished from a subsequent transition state,

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TS2, where H2 has shifted marginally towards the side bound H3. The exchange proceeds without a further stationary point the new dihydrogen H2-H3 being formed and leaving the molecule with H1 bound in the frontal position.

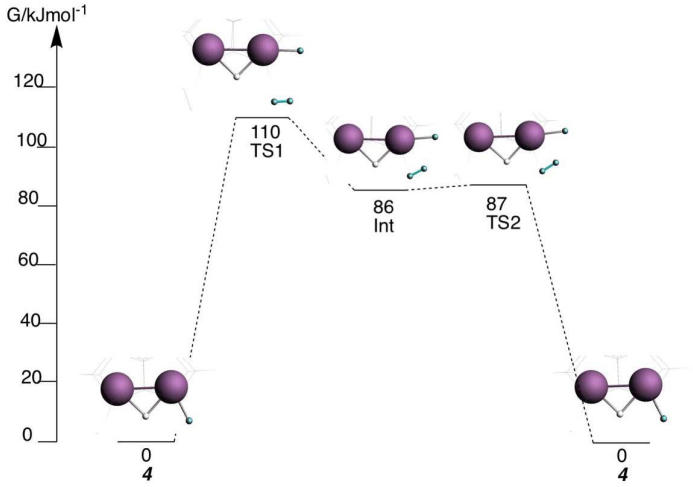

Figure 3: Free energy profile for H exchange between ***4*** and H_2; the exchanging Hs are highlighted.

Table 1. H-H and Ti-H distances (Å) and Ti-Ti-H3 angle (°) for ***3***, **TS1, Int,** and **TS2.**

	H1-H2	H2-H3	Ti-H1	Ti-H2	Ti-H3	Ti-Ti-H3
3					1.75	116
TS1	0.76	2.48	2.56	2.79	1.78	189
Int	0.81	1.73	1.95	1.94	1.80	191
TS2	0.82	1.69	1.94	1.93	1.81	186

The activation energy of the two processes for exchange, one where both H are exchanged, going *via* (**3**) and the one described above where only the terminal H is exchanged, are similar. In order to generate the full range of isotopomers as is demonstrated by the experiments described above both processes must come into play as shown in Figure 4.

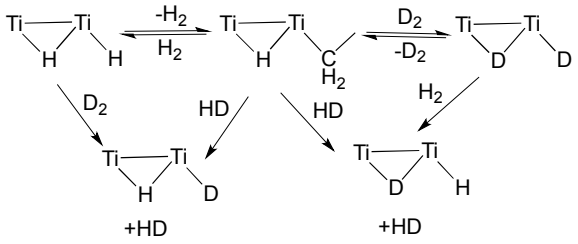

Figure 4: Summary of exchange processes

Reactivity of (**3**) with ^{t}BuCCH and with protic acids:

We next turned our attention to the reactivity of (**3**) with substrates bearing acidic protons, as well as with Bronsted acids (Scheme 4). Reaction of (**3**) with one equivalent of ^{t}BuCCH results in a very clean reaction, furnishing a new complex (**7**) in 100% spectroscopic yield. ^{1}H-NMR spectroscopy was again very informative as it displayed the existence of 8 aromatic pentalene environments and importantly the existence of a bridging hydride, as evidenced by a sharp singlet at -8.83 ppm (δ C_6D_6).

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Furthermore, a sharp singlet at 1.37 ppm integrating for 9H and attributed to the ^{t}Bu group of the alkyne was observed. The $^{13}C\{^1H\}$-NMR spectrum confirmed that the NHC was still coordinated (196.74 ppm) while the DEPT-135 NMR spectrum confirmed that the methyl group that has 'tucked-in' in (**3**) had been reconstituted. Finally, the $^{29}Si\{^1H\}$-NMR spectrum displayed four signals centred at 1.61, 1.85, 2.28 and 3.22 ppm (δ C_6D_6) (0.28, 2.26, 2.97 and 4.94 ppm in (**3**), (δ C_7D_8)). Crystals of (**7**) suitable for a single crystal XRD analysis (Figure 5), revealed its molecular structure, which, based on the spectroscopic data detailed above, is retained in solution.[28]

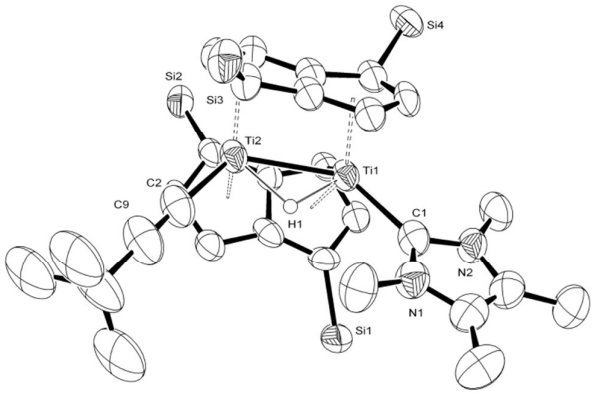

Figure 5: ORTEP diagram of the molecular structure of (**7**) showing 50% probability ellipsoids (H atoms and ^{i}Pr groups have been removed for clarity). Selected bond Lengths (Å) and angles (°): Ti1-Ti2: 2.5753(14), Ti1-C1: 2.267(7), Ti1-H1: 1.83(4), Ti2-H1: 1.81(5), Ti2-C2: 2.150(8), C2-C9: 1.212(11); Ti2-C2-C9: 173.7(6), Ti2-H1-Ti1: 90.3(19), H1-Ti2-Ti1: 45.2(14), H1-Ti1-Ti2: 44.8(14).

The structure shows that (**7**) is the result of C-H activation of the (relatively acidic) alkynic C-H bond in ^{t}BuCCH, which results in bridging hydride and terminal acetylide ligands. The Ti-C(carbene) distance in (**7**) is shorter than the one found in (**3**) (2.300(2) Å)9 but still in the range of 2.2-2.35 Å reported for other Ti-NHC complexes.[29] The two Ti-H bond lengths in (**7**) are the same within esd's but in comparison to the corresponding Ti-H distances found in (**3**), the (NHC)Ti-H distance in (**7**) is longer (1.72(3) Å in (**3**)), whereas the (*C*)Ti-H (*C* = CH_2 in (**3**), CC^{t}Bu in (**7**)) distances are similar within esd's (1.79(3) Å in (**3**)). This causes the Ti-H-Ti bond angle in (**7**) to reduce by 3.1° to 90.3(19)° (93.4(13)° in (**3**)). The C2-C9 bond distance in (**7**) is typical of a C-C triple bond and is in agreement with structurally characterised complexes of the type $Cp^R{}_2Ti(C{\equiv}CR')_2$ (**8**), and the same invariance applies to the Ti-C-C bond angle.[30,16] On the other hand, the Ti-C2 (2.150(8) Å) bond length is longer than ones previously observed (2.108-2.08 Å) in metallocenes of type (**8**), which results in the relief of steric congestion between the bulky Si^{i}Pr$_3$ and ^{t}Bu groups. [30,16]

In order to gain some further insight into the origin of the bridging hydride in (**7**), (**3**) was reacted with ^{t}BuCCD (95% deuterium enriched). Analysis by ^{1}H and ^{2}H-NMR spectroscopy showed *ca* 90% incorporation of deuterium in the hydridic position.[31] This suggests that the predominant pathway for the formation of (**7**) is not *via* the direct protonation of the Ti-CH_2 metallacycle by the acidic H of the terminal alkyne. One possible explanation, and one that is in-line with the observed pressure dependence in the formation of (**4**) (Scheme 2) and the D_2/H_2 exchange discussed earlier, is the formation of a C-H alkane complex that, due to the steric congestion, forces the bridging hydride in (**3**) to migrate onto the Ti-CH_2 bond.

Encouraged by the isolation of (**7**), we decided to investigate the reactivity of (**3**) with Bronsted acids. When an Et_2O solution of (**3**) was reacted with 1 eq of HCl (2.0M solution in Et_2O) at 0 ˚C, an

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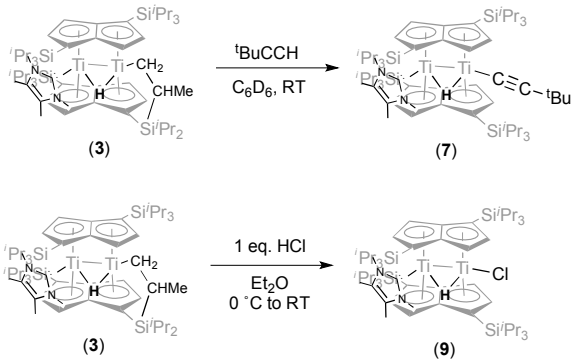
immediate colour change from a dark pine-green solution to a less intense green was observed. NMR spectroscopy after work-up of the reaction mixture, showed the clean formation of a new complex (**9**), which displayed 8 aromatic pentalene environments as well as the existence of a bridging hydride as evidenced by a sharp signal at -8.60 ppm (δ C_6D_6). Furthermore, the $^{13}C\{^1H\}$-NMR spectrum confirmed that the NHC was still coordinated (195.46 ppm), while no secondary carbons were observed in the DEPT-135 spectrum. The $^{29}Si\{^1H\}$-NMR spectrum consisted of four peaks found at 3.28, 2.61, 2.14 and 2.02 ppm (δ C_6D_6). Although mass-spectrometry was uninformative, combustion analysis was consistent with the empirical formula [(NHC)TiHTi{($\mu,\eta^5:\eta^5$)$Pn^\dagger$}$_2$Cl] (**9**) (Scheme 4).



Scheme 4: Reaction of (**3**) with E-H bonds.

Crystals of (**9**) are readily obtained from n-pentane, and the molecular structure (Figure 6) in the solid state is in agreement with our spectroscopic and analytical data. Unfortunately, due to the high mosaicity of the crystals and their sensitivity to long exposure times, we were unable to obtain data of sufficient quality to discuss bond lengths and angles, despite our best efforts; thus, the ORTEP diagram in Figure 6 serves only as confirmation of connectivity.[32]

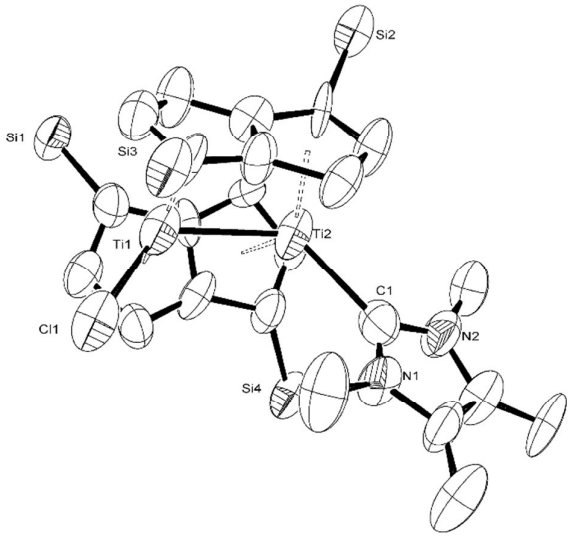


Figure 6: ORTEP diagram of (**9**) displaying 50% probability ellipsoids (H atoms and ^{i}Pr groups have been removed for clarity; two molecules are found in the asymmetric unit).

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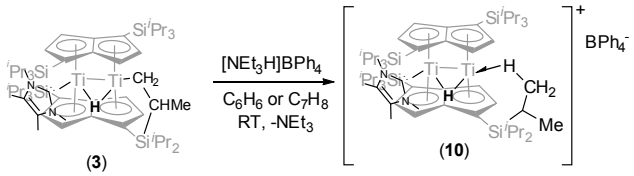
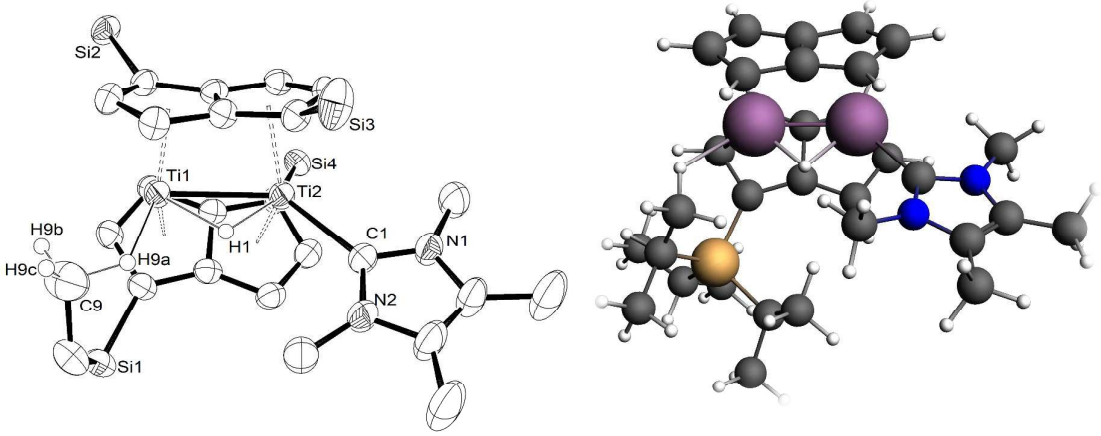
The existence of a bridging hydride in (**9**), encouraged us to pursue the reactivity of (**3**) with other acids, but containing non-coordinating anions. The reaction of (**3**) with 1 eq of $[NEt_3H]^+BPh_4^-$ in toluene or benzene, followed by removal of volatiles produced the new complex (**10**) (Scheme 5) very cleanly, as evidenced by NMR spectroscopy. As in the case of (**9**), 8 pentalene aromatic protons were observed and most importantly a hydride peak at -5.72 ppm (δC_6D_6) which is shifted upfield compared to (**9**), (**7**) and (**4**), as would be expected for a cationic compound. Similarly, a peak at 185.76 ppm in the $^{13}C\{^1H\}$-NMR spectrum confirmed that the NHC was still coordinated, while the DEPT-135 showed no secondary carbons. Furthermore, the $^{13}C\{^1H\}$-NMR spectrum contained a 1:1:1:1 quartet centred at 165.25 ppm assignable to the BPh_4^- counterion ($^1J_{BC}$ = 49.6 Hz), confirming the formation of a cationic species, which was further corroborated by the $^{11}B\{^1H\}$-NMR spectrum consisting of one sharp peak at -6.75 ppm. Finally, the $^{29}Si\{^1H\}$-NMR displayed 4 peaks and is again consistent with a syn-bimetallic complex with two inequivalent $Pn^\dagger$ ligand scaffolds. Crystals suitable for an XRD study were grown by slow diffusion of n-heptane into a toluene solution of (**10**). Figure 7A shows the cation in the molecular structure of (**10**).



Scheme 5: Formation of (**10**) showing agostic interaction



(A) (B)

Figure 7: (A) ORTEP diagram of the cation in the molecular structure of (**10**), displaying 50% probability ellipsoids (selected H atoms and ^{i}Pr groups have been removed for clarity). Selected bond lengths (Å) and angles (°): Ti2-C1: 2.260(2), Ti1-Ti2: 2.5467(6), Ti2-H1: 1.67(3), Ti1-H1: 1.73(3), Ti1-H9A: 2.19(4) C9-H9a: 1.07(4), C9-H9b: 1.02(4), C9-H9c: 1.00(4); Ti1-H1-Ti2: 96.9(16), H1-Ti1-H9A: 70.7(15), Ti2-Ti1-H9A: 111.4(11), Ti1-H9A-C9 121(3). (B) Geometry optimised structure of (**10**).

As can be seen from Figure 7, the most salient feature in the cation of (**10**) is the interaction between hydrogen H9A and the Ti1 metal centre. The Ti1-H9A distance of 2.19(4) Å as well as the angle of Ti1-H9A-C9 (*ie* the methyl carbon attached to H9A/B/C) of 121(3)° suggest that this interaction

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should be classed as agostic (hydrogens a/b/c and H1 were found in the Fourier difference map and refined freely[28]).2c,33 The C9-H9a/b/c bond lengths are similar within esd's and they are all characteristic of C-H bond lengths found in agostic complexes that have been structurally determined by means of neutron diffraction and are within the range of 0.97-1.18 Å.[34,]2c,36 Thus, each Ti centre achieves an eighteen electron count according to the CBC model.[35] Geometry optimisation of a model cation with just one Si^iPr_3 substituent (***10*** = **[**$Ti_2Pn(C_8H_5Si^iPr_3)(\mu\text{-}H)(C_3N_2Me_4)]^+$, Figure 7B) led to an agostic structure with a Ti-H distance of 2.19 Å and a lengthened C-H bond of 1.12 Å, and the calculated Ti-H-C angle of 126º is in fair agreement with the crystallographically determined one. The associated C-H stretching vibration was calculated to be low at 2760 cm^{-1}; [27] this value is almost identical to the experimentally observed value of 2753 cm^{-1} observed for the agostic interaction in (**10**) (thin film), and which is in agreement with previously reported values.[36]

In solution, a doublet at 0.2 ppm ($\delta(C_7D_8)$, integrating for 6H) in the ^{1}H NMR spectrum of (**10**) is the furthest upfield shift for the methyls of the Si^iPr_3 region in the series of complexes reported herein. The $^1J_{CH}$ coupling constant was found[37] to be 124 Hz at 30 ºC, dropping to 112 Hz at -55 ºC and is a good indication of the existence of a fluxional agostic interaction in solution.2c,38 In terms of other pertinent metric parameters, the Ti-H-Ti bond distances in (**10**) are the same within esd's to the ones found in (**3**), (**4**)9 and (**7**) (see above), while the Ti-H-Ti angle is more obtuse than the ones in (**3**) (93.4(13)°), (**4**) (89(2)°) and (**7**) (90.3(19)°). The Ti-NHC bond in (**10**) is also significantly shorter compared to (**3**) and (**4**) but the same within esd's compared to (**7**). Finally, the Ti-Ti bond in (**10**) is slightly lengthened compared to (**4**) (2.5413(8) Å) but shorter than the ones found in (**3**) (2.5610(8) Å) and (**7**) (2.5750(14) Å), possibly as a result of the reduced steric environment around the second Ti centre in (**10**) compared to (**4**) and (**7**)). Unfortunately (**10**) shows no evidence of reactivity with H_2, even up to an overpressure of 3.5 bar.

Conclusions:

In summary, in this paper we report further experimental and theoretical data supporting that the reaction of (**3**) with H_2 reversing the C-H activation to yield (**4**) does not proceed *via* σ-bond metathesis. Moreover, we highlight the importance of the shape and the pKa of the base in promoting the formation of (**3**), and as a result report the first example of the oxidative addition of the C-Cl bond in 2,6-dichloro-pyridine across the Ti=Ti bond in (**1**) to yield a metallaziridine syn-bimetallic Ti_2 core.

The reaction of (**3**) with a substrate bearing an acidic proton, *viz.* ^{t}BuCCH, results in C-H activation and formation of an acetylide hydride. Deuterium labelling studies using ^{t}BuCCD support a mechanism in which the bridging hydride in (**3**) 'hops' back onto the cyclometallated C-H bond when the alkynic C-H bond in ^{t}BuCCH approaches the Ti centre in (**3**), as is the case when (**4**) is produced from the reaction of (**3**) with H_2. The conservation of the Ti-H-Ti syn-bimetallic motif in (**3**) is observed in its reactivity with acids; in the case of the reaction of (**3**) with $[NEt_3H]BPh4$, we were able to isolate complex (**10**) that features an agostic interaction.

Conflicts of Interest:

There are no conflicts of interest to declare

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[31] ^{2}H-NMR spectroscopy also revealed some incorporation in the Si^{i}Pr3 position (<5%). Unfortunately, we cannot unambiguously assign these positions due to (a) the complexity of the spectrum in this region and (b) the minute amounts that these isotopomers are formed thus hindering analysis by $^{13}C\{^1H\}$-NMR, DEPT-135 and other correlation experiments.
[32] The data is 71% complete to a resolution of 0.98 Å. The data was collected using the 'What Is This' functionality within the CrysAlis^{PRO} (Rigaku O. D. 2016) software suite. Solution (ShelXT, Sheldrick 2015) and refinement (Shelx, Sheldrick 2015) were handled through the Olex2 program suite. Residual electron density peak between the two Ti centres can be found at the difference map of this data-set, and it corresponds to the bridging hydride and was refined freely. Although its topology is in very good agreement with (**3**), (**4**) as well as (**7**), and ^{1}H-NMR spectroscopy unambiguously confirms its existence, it is not included in the ORTEP diagram in Figure 4, due to the quality of the data. Crystal data for (**9**): Green needle, 0.01 x 0.02 x 0.08; Molecular Formula: $C_{59}H_{105}ClN_2Si_4Ti_2$; a = 15.863(4) Å, b = 20.452(4) Å, c = 20.552(5) Å, α = 79.849(19)˚, β =77.59(2)˚, γ =76.639(19)˚, V = 6279; Triclinic *P-1*; Z = 4; R_{int} = 8.16%, *R1* = 9.29 %, *wR2* = 23.61%.

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[37] It was indirectly measured *via* a coupled gHSQC 2D correlation experiment.
[38] No change in chemical shift of the hydride peak or the peak at 0.2 ppm was observed down to -70 ºC. Unfortunately, due to the ionic nature of (**10**) and the use of C_7D_8 (with 50 µL of o-$F_2C_6H_4$, otherwise below -20 ºC of the sample suffers precluding further cooling) as solvent, below -60 ºC, the compound starts oiling out of solution resulting in poor shimming and precluding further meaningful characterisation. Solvents like d^8-THF react with (**10**) as observed by an instant colour change to an even darker turquoise colour and significant changes in the ^{1}H-NMR spectrum with most prominent the disappearance of the peak at 0.22 ppm. This is most likely due to the disruption of the agostic interaction due to the coordination of THF on this Ti centre. Nevertheless, extensive drying of a solution of (**10**) exposed to THF reverts the process.

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Formation of an agostic hydrogen by protonation of a "tucked-in" bis(pentalene)ditanium complex